Nanoscale Infrared Spectroscopy of Materials by Atomic Force Microscopy


INTRODUCTION

Atomic force microscopy (AFM) has been enormously successful addressing problems in basic nanoscale research as well as applied problems in materials science and engineering. A clear gap in AFM capabilities, however, is the ability to chemically characterize regions of the sample. This is especially important in the study of heterogeneous materials like polymer blends, multilayer films, nanocomposites and many other areas.

Several AFM probe-based techniques have been used to exceed the diffraction limit of conventional infrared (IR) measurements. Traditional IR microscopy has a resolution limit roughly three times the incident wavelength [1], on the scale of several to tens of micrometers. Various optical scattering methods attempt to relate spectral optical properties of materials to their chemical composition [2,3]. However, in general, nearfield approaches are single or narrow band and do not produce rich spectra that can be used to characterize a broad range of vibrational resonances associated with different chemical species. Other IR techniques are based on measuring local temperature rise from spectral absorption through the use of AFM cantilevers integrated with conventional Fourier transform IR (FTIR) spectrometers [4,5]. These approaches allow broader spectrum measurement than nearfield approaches, but the spatial resolution is typically limited due to thermal diffusion to the scale of many micrometers.

We have developed and implemented a novel lab-based instrument that combines atomic force microscopy and infrared spectroscopy to enable chemical characterization of polymer and other samples at scales below the diffraction limit. The instrument employs photothermal induced resonance (PTIR) that uses an AFM probe to measure local thermal expansion from IR light incident upon a sample. The PTIR technique was originally developed by Dazzi et al. [6-9] using the CLIO free electron source facility at Université Paris-Sud. To make this capability more broadly available, we have developed an instrument based on a lab-scale IR source.

As shown in Figure 1, the sample is illuminated with the pulsed tunable IR laser light source. When IR radiation is absorbed by the sample, the temperature rise from spectral absorption through the use of AFM cantilevers integrated with conventional Fourier transform IR (FTIR) spectrometers [4,5]. These approaches allow broader spectrum measurement than nearfield approaches, but the spatial resolution is typically limited due to thermal diffusion to the scale of many micrometers.

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sample, it creates a rapid thermal expansion wave that excites resonant oscillations of the AFM cantilever. By measuring the amplitude of the cantilever vibrations as a function of the IR source wavelength, a local IR absorption spectrum can be created.

MATERIALS AND METHODS

Materials
Several polymer materials were used in these experiments, including a polymer blend, a multilayer film and a dropcast film. The polymer blend is a 50/50 blend of polycarbonate/acrylonitrile butadiene-styrene (PC/ABS) that was developed for automotive applications. The multilayer film of the type A-B-A and nominal layer composition and thickness are given in Table 1. The polystyrene was drop cast from solution at a concentration of 5 mg ml⁻¹.

Sample Preparation
Samples are prepared on ZnSe prisms in one of two ways. For many samples we employ ultramicrotomy to cut sections with thicknesses between 100 nm and 1000 nm and then we transfer the sections to a prism surface. In other sample preparations we cast thin films from solvent directly on the prism.

Atomic Force Microscopy
Measurements were performed on a custom built AFM/IR spectroscopy platform using contact mode AFM and contact resonance imaging modes. We have used both standard silicon contact mode cantilevers (nominal spring constants ~0.2 N m⁻¹) and Anasys ThermalLever self-heating probes. We also employed novel enhanced resonance probes [11].

Infrared Instrumentation
The new compact IR source is based on a cascaded optical parametric oscillator [10], pumped by a nanosecond diode-pumped 1-µm Nd:YAG laser, and is continuously tunable from 2.5 µm to 10 µm (4000 to 1000 cm⁻¹). This covers a major portion of the mid-IR including important CH, NH and CO bands, as well as carbonyl and amide I and II bands. The spectral width of the IR source is less than 16 cm⁻¹ over the range between 1200 and 3600 cm⁻¹. The sample is mounted (Figure 1) on a zinc selenide (ZnSe) prism and the IR beam is arranged to illuminate the sample by total internal reflection similar to the attenuated total reflection (ATR) technique employed in IR spectroscopy. This arrangement reduces stray light that could cause background absorption in the probe if illuminated from above.

The cantilever deflection is recorded with a traditional AFM optical lever system with a detection bandwidth of roughly 2 MHz. A high speed data acquisition system records each cantilever ring-down event. The IR source is pulsed at ~1 kHz repetition rate and we typically synchronously average multiple ring-downs (e.g. 256) to improve the measurement sensitivity. With measurement and tuning time, each spectrum currently takes roughly one minute. The IR source can also be tuned to a single wavelength and the absorption at that wavelength can be spatially mapped over the sample.

The co-averaged ring-down events are analyzed to extract both IR absorption and mechanical properties. The ring-down events typically include one or more “contact resonances”, i.e. modes of oscillation that couple the cantilever’s resonant properties with the mechanical stiffness and damping of the sample area in contact with the AFM tip. The peak amplitude of the ring-down and/or the amplitude of one or more contact resonance modes is extracted for each wavelength to construct an absorption spectrum. The contact resonant frequencies can be used to extract relative stiffness and sample viscosity.

Table 1: Multilayer film structure.
RESULTS

Polymer Samples
We have used PTIR to measure and map a variety of polymer samples. Figure 2 shows measurements performed on a blend of polycarbonate (PC) and acrylonitrile butadiene styrene (ABS). These materials are employed commercially for properties including high flow for molding, heat resistance and toughness. Polymer blends like these are used in many applications including automotive and consumer electronics. We used PTIR to measure a series of spectra in the CH stretch region while moving the AFM tip 33 nm between each spectrum. The resulting line spectral map shows the spatially resolved IR absorption as a function of the excitation IR frequency (in wavenumbers) and position on the sample. Local chemical variations in this sample are clearly resolved via the change in the position of the CH peak between 2920 and 2970 cm⁻¹ as the tip moves from PC to ABS domains.

The PTIR technique was also used to create a chemical map across the interface of a laminated multilayer film. Multilayer polymer films are becoming widely used in many commercial applications including food and beverage packaging, adhesive layers, surface coatings, electronic displays and organic photovoltaics. High resolution PTIR analysis was performed on an interface of a laminated film of ethylene acrylic acid (EAA) copolymer and Nylon (a polyamide material), as shown in Figure 3. For the wavelengths used in this measurement (~3 µm), the diffraction limit of IR microscopy would be around 10 µm, roughly the entire width of the Nylon layer and twice the field of view of Figure 3. Using the PTIR technique with spectra measured every 50 nm, this line spectral map in Figure 3 clearly resolves the interface on a scale well below the diffraction limit of conventional IR microscopy.

Comparison with Bulk FTIR Analysis
We have compared measurements with the PTIR technique to bulk FTIR measurements. Figure 4 shows example measurements that have been performed on a variety of polymer films with both FTIR and PTIR. Despite the fact that the PTIR measurements are performed on length scales orders of magnitude smaller than bulk FTIR, the measurements exhibited generally good correlation between FTIR and PTIR.

Mechanical and Thermal Analysis
The PTIR technique can also provide simultaneous mechanical and thermal property mapping along with chemical analysis. When an IR pulse is absorbed by the sample, the rapid thermal expansion induces resonant oscillation of the cantilever. The frequencies of oscillation, called contact resonances [12,13], are dependent on the contact stiffness of the sample directly under the AFM tip. As illustrated in Figure 5, contact resonances shift to higher frequencies on harder materials and vice versa. Recent progress has been made in extracting quantitative measurements of elastic and viscous properties of materials by analyzing these cantilever contact resonances [14].

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Figure 6 shows measurements of topographic, chemical, mechanical and thermal properties performed on the multilayer sample shown in Figure 3. The mechanical and spectroscopic data were obtained simultaneously, thus allowing direct correlation of mechanical stiffness information with chemical composition data. Note that the transitions in contact stiffness correlates extremely well with the strength of the CH absorption. Nano-thermal analysis [15] was also performed on the same sample clearly identifying softening at different temperatures for the Nylon and EAA layers.

DISCUSSION

The correlation of structure and function is of critical importance to materials science and engineering at the nanoscale. With the PTIR technique, we have demonstrated the ability to measure spatially resolved topographic, chemical, mechanical and thermal properties. The nanoscale resolution of these measurements operates well below the diffraction limits of conventional IR spectroscopy. Further these measurements can be performed either simultaneously and/or with the same probes on the same samples. As a result, it is possible to measure and study materials with greater richness and spatial resolution than previously available. Because of the high correlation to FTIR spectra, the PTIR technique can leverage the enormous existing materials databases of IR absorption reference spectra. We have exported PTIR spectra into Bio-Rad’s KnowItAll spectral analysis and successfully identified unknown materials via correlation with IR absorption databases.

CONCLUSION

We have demonstrated the application of PTIR that combines infrared spectroscopy and atomic force microscopy to provide high resolution topographic, chemical, mechanical and thermal mapping. This combination provides spatial resolution at length scales well below the diffraction limit of conventional IR spectroscopy and adds chemical spectroscopy to the field of atomic force microscopy.

REFERENCES

1. See for example: www.thermo.com/eThermo/CMA/PDFs/Articles/articleFile_7208.pdf